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**(54) TREATMENT OF  
CHLOROPHENOL-CONTAINING WATER**

(57) Abstract:

**PROBLEM TO BE SOLVED:** To make chlorophenol efficiently harmless at a low cost by treating a chlorophenol-containing water with a phenol oxidation enzyme and a bio-degrading flocculant having an amino group to flocculate chlorophenol and then applying anaerobic biological treatment to the flocculated material.

**SOLUTION:** In the case of treating the chlorophenol-containing water discharged from synthetic organic

chemical factories, the chlorophenol-containing water is made harmless by treating with the phenol oxidation enzyme and the bio-degrading flocculant at first to flocculate chlorophenol and after that, applying anaerobic biological treatment. At this time, as the phenol oxidation enzyme, preferably tyrosinase, laccase or the like, as the bio-degradative flocculant having the amino group, preferably a cationic modified material such as chitin are used. And as the treating condition, one prepared by dissolving the phenol oxidation enzyme in the concentration of  $\geq 1$ mg/ml is added make the concentration of 0.01-100U/ml.

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**[Claim(s)]**

[Claim 3] The art according to claim 1 or 2 whose biodegradability flocculant which has an amino group is a chitin, a chitin partial deacetylation object, chitosan, or the cation denaturation object of albumin.

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## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the new art of chlorophenols content water. If it says in more detail, this invention relates to the practical art of the chlorophenols content water which makes chlorophenols harmless at few cost efficiently by giving chlorophenols content water combining the specific processing and specific anaerobe processing by the enzyme and the flocculant.

[0002]

[Description of the Prior Art] Although various chlorophenols are contained in drainage which comes out of a synthetic organic chemical plant, a pulp mill, etc. and an adsorption process, an extraction method, an ion-exchange method, an oxidation style, biological treatment, coagulating sedimentation, etc. have been conventionally examined by processing of these drainage, only an activated sludge process and coagulating sedimentation are performed practical from fields, such as an effect and economical efficiency. However, in an activated sludge process, biodegradability of chlorophenols is low, and there is a fault that biodegradation is not fully carried out from biological activity being checked since it moreover has toxicity, and in coagulating sedimentation, since it is hard to condense a low-molecular organochlorine compound like chlorophenols, it has the fault of being easy to be emitted into environment, without being removed. Therefore, development of the art of the chlorophenols content water which makes underwater chlorophenols harmless efficiently is desired.

[0003] The art using a phenolic-acid-ized enzyme is thought as an effective art of the chlorophenols which are a low-molecular organochlorine compound, the flocculant which has a phenolic-acid-ized enzyme and an amino group is used together until now, and the method of carrying out the coagulation treatment of phenols or the aniline is proposed (JP.6-102200,B). However, since the oxidation polymerization of the chlorophenols is carried out and it is condensed, without decomposing when this method is applied to processing of chlorophenols, the aggregate contains an organochlorine compound and causes secondary pollution.

[0004]

[Problem(s) to be Solved by the Invention] this invention is the basis of such a situation and is made for the purpose of offering the practical art of the chlorophenols content water which may turn harmless at few cost efficiently in chlorophenols content underwater chlorophenols.

[0005]

[Means for Solving the Problem] The aggregate obtained by using together and processing the biodegradability flocculant which has a phenolic-acid-ized enzyme and an amino group for chlorophenols content water finds out making it harmless easily by anaerobe processing, and this invention persons came to complete this invention based on this knowledge, as a result of repeating research wholeheartedly that the practical art of chlorophenols content water should be developed.

[0006] That is, the art of the chlorophenols content water characterized by making this invention harmless by processing chlorophenols content water by the biodegradability flocculant which has a phenolic-acid-ized enzyme and an amino group, making chlorophenols condense, and subsequently carrying out anaerobe processing of this aggregate is offered.

[0007]

[Embodiments of the Invention] As chlorophenols content water with which this invention method is applied, one sort or the thing contained two or more sorts is mentioned, for example in the chloro substitution product of phenols, such as a chlorophenol, a chloro methoxy phenol, chlorocresol, and a chloro hydroxy phenol. There is especially no limit about the concentration of this content underwater chlorophenols.

[0008] As a phenolic-acid-ized enzyme used in this invention method, a tyrosinase, a laccase, a peroxidase, a polyphenol oxidase, etc. are mentioned, for example. This tyrosinase, a laccase, etc. serve as a catalyst at the time of oxidizing phenols under oxygen existence (good in air), and, on the other hand, a peroxidase etc. serves as a catalyst at the time of oxidizing phenols under hydrogen-peroxide existence. About the origin, especially a limit does not have these enzymes, and they may originate in any of an animal, vegetation, and a microorganism. Moreover, the extract of the animal which these enzymes may use a commercial enzyme preparation, or contains a desired enzyme, vegetation, and a microorganism may be used, for example, a mushroom etc. can also be used as a tyrosinase and a Western Japanese horseradish etc. can also be used as a peroxidase. Moreover, as long as it is a request, you may use combining two or more sorts of enzymes.

[0009] On the other hand, the biodegradability flocculant which has an amino group is a flocculant which has glycan structure and the chemical structures which are easy to biodegrade, such as peptide structure etc., and has an amino group, and protein, such as an amino derivative of polysaccharide, such as a partial deacetylation object of a chitin and a chitin and chitosan, or a cation denaturation object of albumin, the cation denaturation object of those, etc. can be mentioned as such a thing, for example. These flocculants may be used independently and may be used combining two or more sorts.

[0010] The biodegradability flocculant which has the aforementioned phenolic-acid-ized enzyme and an amino group is first used together, chlorophenols content water is processed, and these chlorophenols are made to condense in this invention.

[0011] Under the present circumstances, as for a phenolic-acid-ized enzyme, as processing conditions, it is advantageous to add what was dissolved in the concentration of 1mg/ml or more so that it may usually become 0.01-100U/ml concentration. On the other hand, although it is good to decide by performing a preliminary test beforehand in relation to the concentration of chlorophenols as for the addition of a flocculant, it is usually chosen in the 0.1-100mg [l.] range. In addition, you may fix and use the aforementioned phenolic-acid-ized enzyme for support. 10-50 degrees C of processing temperature are usually preferably chosen in 20-40 degrees C. Moreover, the ranges of pH are usually 4-8, and it is suitably chosen according to the kind of enzyme to be used. For example, in a peroxidase, the pH 7 neighborhood is [ at the pH 5.5 neighborhood and a laccase ] the optimal in the pH 4 neighborhood and a tyrosinase.

[0012] In order to promote a reaction, an assistant may be added to the case of the chlorophenols which cannot oxidize easily with a phenolic-acid-ized enzyme, and the oxide and chlorophenols of polymerization may be made to carry out to it by request in this invention. For example, in the case of a tyrosinase (mushroom origin) and a peroxidase (Western Japanese horseradish origin), it is advantageous to add a phenol etc. as an assistant.

[0013] Moreover, when using a peroxidase as an enzyme, addition of a hydrogen peroxide is required, and since it needs oxygen for oxidation reaction on the other hand in using a laccase and a tyrosinase, it is good to stir in air or to carry out aeration of oxygen or the air. Moreover, you may make a chemical reaction etc. generate these hydrogen peroxides and oxygen in the system of reaction.

[0014] In this invention, although the aforementioned flocculant may be begun, and may be added in shell processed water and you may add in the back in the middle of oxidation treatment by the phenolic-acid-ized enzyme, as for this addition time, it is good to choose suitably according to the kind of enzyme to be used. For example, since deactivation is late, although the back in the middle of oxidization is available for addition of a flocculant, since it combines with the oxide of phenols immediately and deactivates, in order to prevent it, it is advantageous [ in the case of a peroxidase, ] in the case of a laccase or a tyrosinase, to begin and to add a shell flocculant in processed water.

[0015] Since processed underwater chlorophenols condense by such processing, well-known meanses, such as filtration, centrifugal separation, precipitation separation, and floatation, separate this aggregate.

[0016] In this invention method, anaerobe processing is performed and made harmless to the aggregate obtained by doing in this way. This anaerobe processing is the method of disassembling the organic substance into methane and a carbon dioxide using the microorganism which works in the state of an anaerobiosis without oxygen. As conditions for this anaerobe processing, the temperature of 30-40 degrees C, pH 6-8, and the sludge concentration of 3,000-30,000mg/l. are the optimal.

[0017]

[Effect of the Invention] According to this invention method, these chlorophenols can be efficiently made harmless by giving chlorophenols content water combining the processing and anaerobe processing by the combined use of a biodegradability flocculant which has a phenolic-acid-ized enzyme and an amino group.

[0018] Therefore, the art of the chlorophenols content water of this invention is a method that practical value

is high, for example, is applicable to a water treatment process, the industrial water processing, waste water treatment, waste leachate processing, etc.

[0019]

[Example] Next, although an example explains this invention to a detail further, this invention is not limited at all by these examples.

[0020] 30ml (sewage digested sludge currently cultivated by the glucose) of manufacture aversion sludge of example 1 (1) chitosan habituation sludge. When the anaerobic treatment was performed on pH 7 and conditions with a temperature of 35 degrees C in addition to the chitosan solution of hydrochloric acid containing chitosan 30mg, habituation was carried out in abbreviation 50 days (it is generation and mlvs 10.6g/l. about about 50% of methane), and decomposition took place from the first stage in the 2nd time (mlvs 9.2g/l.) and the 3rd time (mlvs 1.4g/l.).

[0021] (2) The solution containing processing [ of 2, 4, and 5-trichlorophenol ] 2 and 4, 5-trichlorophenol 0.2mM, hydrogen-peroxide 0.3mM, and peroxidase (Wako Pure Chem make, Western Japanese horseradish origin) 0.4U/ml, phosphate buffer solution 10mM (pH 5.5), and the chitosan solution of hydrochloric acid (chitosan concentration of 10mg/l.) was stirred at the room temperature. The chlorophenol elimination factor of 30 minutes after was 100%, and since coagulation sedimentation arose, this coagulation sedimentation object was separated. This precipitate contained and carried out 90 % of the weight (AOX) of adsorptivity organic halogenated compounds.

[0022] Next, when the chitosan habituation aversion sludge obtained above (1) was added so that it might become 3,000mg [l.] concentration, and anaerobe processing was performed at 35 degrees C, generation of the methane by disassembly of a coagulation sedimentation object was immediately seen by this coagulation sedimentation object, and isolation of the chloride ion accompanying decomposition of a chlorophenol was observed after three days, and this aggregate was decomposed into it.

[0023] Like example of comparison 1 example 1, 2, 4, and 5-trichlorophenol was processed by the peroxidase and the synthetic-macromolecule flocculant hexamethylenediamine-epichlorohydrin polycondensation object (10mg [l.] concentration), and the coagulation sedimentation object was obtained. It was not decomposed, although aversion sludge was added like the example 1 in this coagulation sedimentation object and anaerobe processing was performed.

[0024] Like example of comparison 2 example 1, 2, 4, and 5-trichlorophenol was processed by the peroxidase and the aluminum sulfate (200mg [l.] concentration), and the coagulation sedimentation object was obtained. It was not decomposed, although aversion sludge was added like the example 1 in this coagulation sedimentation object and anaerobe processing was performed.

[0025] example of comparison 3o-, m-, p-chlorophenol, 2, 3-, 2, 4-, 2, 5-, 2, 6-dichlorophenol, 2 and 4, 5-, 2 and 4, 6-trichlorophenol, 2, 3 and 4, 6-, 2, 3 and 5, and each 6-tetrachlorophenol -- 0.2mM Although only the chitosan solution of hydrochloric acid was added in the solution to contain so that chitosan concentration might become [ l. ] in 10, 20, 40, 80, 200, and 400mg /, coagulation sedimentation produced neither at all. That is, the chlorophenols themselves cannot be condensed by the flocculant.

[0026] When the solution which contains example 22, 6-dichlorophenol 0.5mM, hydrogen-peroxide 0.6mM, and peroxidase 0.2U/ml, phosphate buffer solution 5mM (pH 5.5), and the 20mg [l.] chitosan solution of hydrochloric acid (as chitosan) was stirred at the room temperature, the chlorophenol elimination factor of 30 minutes after is 99%, and coagulation sedimentation produced it.

[0027] When not adding a flocculant (chitosan solution of hydrochloric acid), the chlorophenol elimination factor of 1 hour after was 29.6%, and even if time passed after that, it was still the same elimination factor. That is, if a flocculant is not added, it is shown that an enzyme deactivates quickly.

[0028] Next, after separating a coagulation sedimentation object, when the chitosan habituation aversion sludge obtained in the example 1 (1) was added so that it might become 6,000mg [l.] concentration, and anaerobe processing was performed at 35 degrees C, generation of the methane by disassembly of a coagulation sedimentation object was immediately seen by this coagulation sedimentation object, and isolation of the chloride ion accompanying decomposition of a chlorophenol was observed after three days, and this aggregate was decomposed into it.

[0029] The solution containing examples 32 and 4, 5-trichlorophenol 0.2mM, hydrogen-peroxide 0.3mM, and peroxidase 0.4U/ml, phosphate buffer solution 10mM (pH 5.5), and a chitin partial deacetylation object solution (this deacetylation object concentration of 10mg/l.) was stirred at the room temperature. The chlorophenol elimination factor of 30 minutes after was 100%, and since coagulation sedimentation arose, this coagulation sedimentation object was separated.

[0030] Next, when the chitosan habituation aversion sludge obtained in the example 1 (1) was added so that

it might become 3,000mg [l.] concentration, and anaerobe processing was performed at 35 degrees C, generation of the methane by disassembly of a coagulation sedimentation object was immediately seen by this coagulation sedimentation object, and isolation of the chloride ion accompanying decomposition of a chlorophenol was observed after three days, and this aggregate was decomposed into it.

[0031] The solution containing examples 42 and 4, 5-trichlorophenol 0.2mM, hydrogen-peroxide 0.3mM, and peroxidase 0.4U/ml, phosphate buffer solution 10mM (pH 5.5), and the cation denaturation object solution (this cation denaturation object concentration of 10mg/l.) of albumin was stirred at the room temperature. Since the chlorophenol elimination factor of 30 minutes after is 100% and coagulation sedimentation produced it, this coagulation sedimentation object was separated.

[0032] Next, when the chitosan habituation aversion sludge obtained in the example 1 (1) was added so that it might become 3,000mg [l.] concentration, and anaerobe processing was performed at 35 degrees C, generation of the methane by disassembly of a coagulation sedimentation object was immediately seen by this coagulation sedimentation object, and isolation of the chloride ion accompanying decomposition of a chlorophenol was observed after seven days, and this aggregate was decomposed into it.

[0033] each example 5p-chlorophenol and 2, and 4-dichlorophenol -- 0.2mM, 2 and 4, 5- and 2 and 4, and each 6-trichlorophenol -- 0.1mM, 2, 3 and 4, 6-tetrachlorophenol 0.02mM, pentachlorophenol 0.01mM, hydrogen-peroxide 1mM, and peroxidase 0.2U/ml, phosphate buffer solution 10mM (pH 5.5), and the 20mg [l.] (as chitosan) chitosan solution of hydrochloric acid When the solution [43 ppm (TOC) of total organic carbons, 45 ppm (AOX) of adsorptivity organic halogenated compounds] to contain was stirred at the room temperature, the elimination factor of the chlorophenol of 30 minutes after is 100%, and coagulation sedimentation produced it. TOC of a treated water was 6 ppm and AOX was 4 ppm.

[0034] Next, after separating a coagulation sedimentation object, when the chitosan habituation aversion sludge obtained in the example 1 (1) was added so that it might become 6,000mg [l.] concentration, and anaerobe processing was performed at 35 degrees C, generation of the methane by disassembly of a coagulation sedimentation object was immediately seen by this coagulation sedimentation object, and isolation of the chloride ion accompanying decomposition of a chlorophenol was observed after 14 days, and this aggregate was decomposed into it.

[0035] Although the elimination factor of the chlorophenols of 10 hours after was 100% when the solution containing example 62, 6-dichlorophenol 0.2mM, and laccase [regulus RATAKE (*Coriolus versicolor*) origin] 5U/ml and phosphate buffer solution 5mM (pH 4) was stirred at the room temperature in air, precipitation was hardly produced. Since coagulation sedimentation arose when it added so that chitosan concentration might become [l.] this solution in 10mg /about the chitosan solution of hydrochloric acid, and stirred, this coagulation sedimentation object was separated.

[0036] Next, when the chitosan habituation aversion sludge obtained in the example 1 (1) was added so that it might become 3,000mg [l.] concentration, and anaerobe processing was performed at 35 degrees C, generation of the methane by disassembly of a coagulation sedimentation object was immediately seen by this coagulation sedimentation object, and isolation of the chloride ion accompanying decomposition of a chlorophenol was observed after three days, and this aggregate was decomposed into it.

[0037] each example 7p-chlorophenol and 2, and 4-dichlorophenol -- 0.2mM, 2 and 4, 5- and 2 and 4, and each 6-trichlorophenol -- 0.1mM, 2, 3 and 4, 6-tetrachlorophenol 0.02mM, pentachlorophenol 0.01mM, and laccase 5U/ml and phosphate buffer solution 5mM (pH 4) Although the elimination factor of the chlorophenols of 10 hours after was 90% when the solution to contain was stirred at the room temperature in air, precipitation was hardly produced. Since coagulation sedimentation arose when it added so that chitosan concentration might become [l.] this solution in 10mg /about the chitosan solution of hydrochloric acid, and stirred, this coagulation sedimentation object was separated.

[0038] Next, when the chitosan habituation aversion sludge obtained in the example 1 (1) was added so that it might become 6,000mg [l.] concentration, and anaerobe processing was performed at 35 degrees C, generation of the methane by disassembly of a coagulation sedimentation object was immediately seen by this coagulation sedimentation object, and isolation of the chloride ion accompanying decomposition of a chlorophenol was observed after 14 days, and this aggregate was decomposed into it.

[0039] Although the elimination factor of the chlorophenols of 5 hours after was 100% when the solution containing example 8p-chlorophenol 0.5mM and tyrosinase (SIGMA company make, mushroom origin) 100U/ml and phosphate buffer solution 5mM (pH 7.0) was stirred at the room temperature in air, precipitation was hardly produced. Since coagulation sedimentation arose when it added so that chitosan concentration might become [l.] this solution in 20mg /about the chitosan solution of hydrochloric acid, and stirred, this coagulation sedimentation object was separated.

[0040] Next, when the chitosan habituation aversion sludge obtained in the example 1 (1) was added so that it might become 3,000mg [l.] concentration, and anaerobe processing was performed at 35 degrees C, generation of the methane by disassembly of a coagulation sedimentation object was immediately seen by this coagulation sedimentation object, and isolation of the chloride ion accompanying decomposition of a chlorophenol was observed after seven days, and this aggregate was decomposed into it.

[0041] Although the elimination factor of the chlorophenol of 1 hour after was 100% when the solution containing 9m-chlorophenol 0.2mM [ of examples ] and tyrosinase 100U/ml, phenol 1.5mM, and phosphate buffer solution 5mM (pH 7.0) was stirred at the room temperature in air, precipitation was hardly produced. Since coagulation sedimentation arose when it added so that chitosan concentration might become [ l. ] this solution in 20mg /about the chitosan solution of hydrochloric acid, and stirred, this coagulation sedimentation object was separated.

[0042] Thus, if independent, a polymerization can be carried out to a phenolic-acid ghost, and it can be made to condense by adding a phenol as an assistant by the flocculant which has an amino group also about the chlorophenols which cannot oxidize easily.

[0043] Next, when the chitosan habituation aversion sludge obtained in the example 1 (1) was added so that it might become 3,000mg [l.] concentration, and anaerobe processing was performed at 35 degrees C, generation of the methane by disassembly of a coagulation sedimentation object was immediately seen by this coagulation sedimentation object, and isolation of the chloride ion accompanying decomposition of a chlorophenol was observed after three days, and this aggregate was decomposed into it.

[Translation done.]